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## FORMATION OF ASSOCIATES FROM NANOSIZED COMPLEXES OF URANIUM IN THE WATER - SUPERCRITICAL CARBON DIOXIDE SYSTEM

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The paper describes the results from studies into the role of water in the formation of associates from nanosized complexes of uranium in a supercritical carbon dioxide (SC CO<sub>2</sub>) medium. It has been demonstrated experimentally that water in the SC CO<sub>2</sub> exists in the form of microdrops. It is found that at a pressure of 10 MPa and a temperature of 40°C the UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2(C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>PO complex may take on hydrophilic properties. The conclusion is made that in that event the mentioned complex would concentrate in water microdrops. The concentration of the complex in water microdrops gives rise to the formation of associates, the size of which is determined by microdrop dimensions.

**KEY WORDS:** supercritical carbon dioxide, supercritical fluid extraction, uranium, water, tributyl phosphate

### УТВОРЕННЯ АСОЦІАТИВ ІЗ НАНОРОЗМІРНИХ КОМПЛЕКСІВ УРАНУ В СИСТЕМІ ВОДА - НАДКРИТИЧНИЙ ДІОКСИД ВУГЛЕЦЮ

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Наведено результати дослідження ролі води в утворенні асоціатів з нанорозмірних комплексів урану в середовищі НК СО<sub>2</sub>. Експериментально показано, що вода в НК СО<sub>2</sub> існує у вигляді мікрокрапель. Відзначено, що при тиску 10 МПа й температурі 40 °С комплекс UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2(C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>PO може придбавати гідрофільні властивості. Зроблено висновок про те, що внаслідок придбання цим комплексом гідрофільних властивостей він буде концентруватися в мікрокраплях води. Концентрування комплексу в мікрокраплях води приводить до утворення в системі асоціатів, розмір яких визначається розміром мікрокрапель.

**КЛЮЧОВІ СЛОВА:** надкритичний вуглекислий газ, надкритична флюїдна екстракція, уран, вода, трибутилфосфат

### ФОРМИРОВАНИЕ АССОЦИАТОВ ИЗ НАНОРАЗМЕРНЫХ КОМПЛЕКСОВ УРАНА В ДВУХФАЗНОЙ СИСТЕМЕ ВОДА - СВЕРХКРИТИЧЕСКИЙ ДИОКСИД УГЛЕРОДА

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Приведены результаты исследования роли воды в образовании ассоциатов из наноразмерных комплексов урана в среде СК СО<sub>2</sub>. Экспериментально показано, что вода в СК СО<sub>2</sub> существует в виде микрокапель. Отмечено, что при давлении 10 МПа и температуре 40 °С комплекс UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2(C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>PO может приобретать гидрофильные свойства. Сделан вывод о том, что вследствие приобретения этим комплексом гидрофильных свойств он будет концентрироваться в микрокаплях воды. Концентрирование комплекса в микрокаплях воды приводит к образованию в системе ассоциатов, размер которых определяется размером микрокапель.

**КЛЮЧЕВЫЕ СЛОВА:** сверхкритический углекислый газ, сверхкритическая флюидная экстракция, уран, вода, трибутилфосфат

Among vital issues in the development of nuclear-power engineering are the nuclear fuel production as well as the reprocessing of spent nuclear fuel (SNF) and uranium industry wastes. However, the advance in this respect is hindered by a number of factors such as the exhaust of raw-material resources base, environmental degradation of uranium industrial estates, and low economic indicators of traditional methods of uranium fuel production and reprocessing due to large quantities of liquid radioactive wastes. Therefore, the elaboration of new, ecologically safe technologies, which would be helpful in avoiding the mentioned problems or in solving them in a new way, is one of the most important tasks of nuclear-power engineering.

Currently, supercritical fluid technologies (SCFT) of extraction are finding increasing use in various spheres of industrial production, e.g., in pharmaceuticals; in fat-and-oil, chemical industries; in coal conversion and petroleum refining. Along with the mentioned applications, the SCFT hold a particular position in SNF and uranium industry waste reprocessing, and also, in the processes of deactivation and selective extraction of actinides [1, 2]. At that, preference is given to supercritical carbon dioxide (SC CO<sub>2</sub>) as an extractant, because it appears a most economical and ecofriendly solvent as compared to those employed in traditional chemical processes. The SC CO<sub>2</sub> is harmless and is noted for its low critical temperature and pressure values, this being of

undeniable advantage. Besides, the technology under discussion makes it possible [3]:

- to reduce considerably the volume of secondary liquid radioactive wastes;
- to give up the use of inflammable, toxic or expensive solvents;
- to carry out pre-separation of extractable compounds at the extraction stage due to an essential change in the solving power of SC CO<sub>2</sub> at insignificant variations in the extractor temperature and pressure;
- to decrease corrosion load on the equipment elements;
- to use water-insoluble selective reagents;
- to reduce essentially the process flow scheme and operating areas of radiochemical facilities.

The presence of small water portions is known to improve the extraction efficiency. It has been demonstrated in [2] that the presence of water is the necessary condition for SC CO<sub>2</sub> extraction of metals. It has been established by experiments that in the absence of water the process of metal extraction is not observed at all. An increase in the quantity of water added up to a certain limit leads to an increase in the efficiency of SC CO<sub>2</sub> extraction of metals. A further increase in the quantity of water added exerts practically no effect on the extraction efficiency.

In [4], it has been shown by theory and experiment that, as in [2], with an increase in the quantity of water the extraction efficiency increases up to a certain peak level. However, after that, as the quantity of added water increases, the extraction efficiency drops. In the opinion of the authors of [4], this drop in the extraction efficiency is due to the following two reasons:

- the existence of water solubility limit in SC CO<sub>2</sub>;
- competition between the uranium complex and pure water on their dissolving in a restricted volume of SC CO<sub>2</sub>.

Though in recent years an array of experimental data has been obtained about the influence of water on the extraction efficiency of uranium complexes (e.g., see refs. [1-3]), some aspects of the problem still remain unclear. Among them, we should mention, first of all, a clear understanding of the structure of the resulting uranyl nitrate+tributyl phosphate (TBP) complex, the description of possible ways of associate formation [5] from nanosized complexes of uranium in the SC CO<sub>2</sub> medium in the presence of microquantities of water, and also, the determination of the form and size of the associates.

Despite the fact that the authors of refs. [6, 7] have analyzed the processes of micelle formation during supercritical fluid extraction of uranium, as well as the processes of spontaneous formation of associates in the SC CO<sub>2</sub> medium during uranium extraction from SNF, their substantiations are not based on a common ground, i.e., the phenomena of micelle formation and associate formation were analyzed as separate processes.

Therefore, the objectives of the present work are to analyze the parameters of a nanosized uranyl nitrate+TBP complex; to describe possible ways of associate formation from nanosized complexes of uranium in the SC CO<sub>2</sub> medium in the presence of microquantities of water; and to determine the form and size of the associates from a unified standpoint.

## EXPERIMENTAL STUDIES ON PHASE STATES IN THE TWO-PHASE WATER-SC CO<sub>2</sub> SYSTEM

The determining influence of the presence of water on the extraction process has been indicated in [2, 4]. Previously, there were reports in the scientific literature about some peculiarities of water solubility in supercritical carbon dioxide (e.g., see [8, 9]). For all that we have made a series of experiments to investigate the phenomenon at the SFE-U facility [4] (modification of SCFE-1 [10]).

From the experimental data reported in [4] it follows that in the pressure range under study (7 to 17 MPa) at a temperature of 40°C the mole fraction of water dissolved in SC CO<sub>2</sub> is practically constant and makes about 0.0054.

So, at a given temperature the supercritical fluid can dissolve only a certain quantity of water, i.e., the supercritical fluid is characterized by the water solubility limit. The excess water remains on a filter paper, and thus cannot participate in the SFE-CO<sub>2</sub> process.

### Laser diffractometry

Along with the evaluation of water solubility in SC CO<sub>2</sub>, the phase state of water dissolved in SC CO<sub>2</sub> was also analyzed.

*In-situ* measurements have been carried out to investigate the phase state of water in SC CO<sub>2</sub> using the SFE-U facility, where at outlet from the reactor, 48.13 cm<sup>3</sup> in volume, there is an optical high-pressure cell (HPC) with sapphire windows. After the extraction has been made, the eluent was discharged into the HPC for investigating its state by optical methods such as laser light diffractometry and optical microscopy. The cell design is shown in Fig. 1.

The water-phase laser diffraction was investigated in accordance with the scheme presented in Fig. 2. The cell was placed in the holder with the outside surface of the HPC sapphire window perpendicular to the laser beam at a distance of no less than 0.5 m from the laser exit aperture. The screen was removed from the cell at the distance  $L=3.3$  m. Along the perimeter of the screen there were two mutually perpendicular rules with 0.5 cm divisions, intended for evaluating the dimensions of diffraction pattern elements.

The spectral range of single-crystalline sapphire window transparency lies within 280 to 1200 nm. The sapphire windows are 10.0 mm in diameter and 6.0 mm in thickness. The windows in the cell are sealed in such a way as to exclude the sapphire-metal contact and to prevent their mechanical failure. Ceramic heaters and a chromel-alumel thermocouple are fastened to the side walls of the cell. The temperature of the cell is maintained with a control device in the range from room temperature to 50°C to an accuracy of  $\pm 1^\circ\text{C}$ . The cell casing is made from stainless steel and is rated for pressures up to 20 MPa. The cell volume is 1.57 cm<sup>3</sup>.

The optical path length of the cell could be varied from 0.1 mm up to 21.0 mm. This could be attained by introducing additional 3.0 mm thick glasses and positioning them at the sapphire window facing the laser beam source.

In the course of experimentation it was established that the water phase in SC CO<sub>2</sub> existed in the form of microdrops. Their dimensions were evaluated from diffraction patterns obtained when passing red laser beam through

the optical HPC. The occurrence of diffraction patterns at laser beam scattering by water microdrops in SC CO<sub>2</sub> is due to the fact that the refraction indices of water and SC CO<sub>2</sub> are different. As is known, the diffractive lattices are formed even in a transparent liquid or gas, where the refraction index is changed by travelling or standing ultrasonic waves [11].

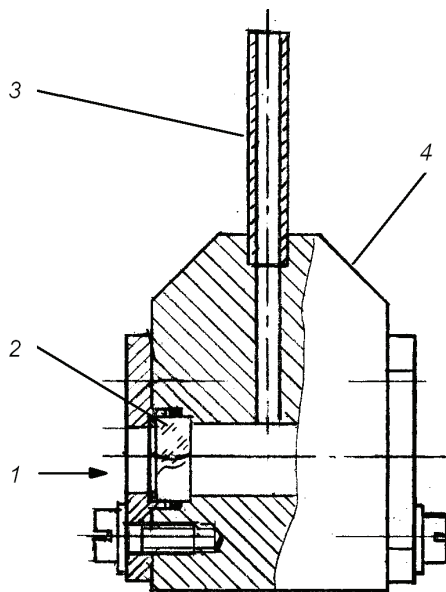


Fig. 1. Design of the optical high-pressure cell.

1 – optical channel; 2 – sapphire window; 3 – inlet/outlet connection; 4 – casing

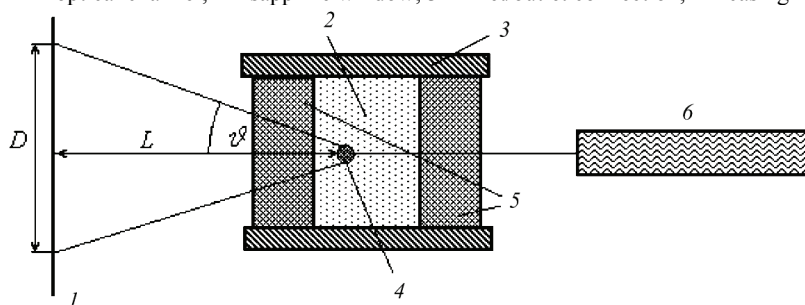


Fig. 2. Diagram of diffraction pattern formation at laser beam scattering by the water microdrops.

1 – screen; 2 – SC CO<sub>2</sub>; 3 – HPC metal casing; 4 – water drop of diameter  $d$ ; 5 – sapphire windows; 6 – laser beam source.

Figure 3 shows one of the images of the static diffraction pattern for the 6.0 mm optical path to the HPC (to reduce the optical path length, 5 glasses were used) at CO<sub>2</sub> pressure of 10.0 MPa and a temperature of 40°C.

Based on a series of the resulting static diffraction patterns, it can be assumed that certain microquantities of water in SC CO<sub>2</sub> form water droplets, which present spherical particles of diameter  $d$  (water drops) distributed in a supercritical fluid. In the pressure range from 8.0 MPa to 16.0 MPa at a temperature of 40°C, in accordance with the phase diagram of CO<sub>2</sub> [12], the weight of water microdrops is greater than the weight of the fluid forced out by the microdrops. For this reason, the microdrops like small shots in oil slowly settle down under the action of gravity, and simultaneously move in convective streams (these being due to the temperature gradient) with changing their position in space. Since the medium is optically transparent, all particles being on the optical path in the cell can be considered as the ones being in the same virtual plane  $P$ . In this case, the analysis of the above-given diffraction pattern is similar to the analysis of diffraction patterns from a two-dimensional grating.

We now describe the experimentally observed evolution of diffraction patterns at laser radiation scattering by water microdrops in the SC CO<sub>2</sub>.

With a red laser, the diffraction pattern image on the screen generally represents slowly moving light spots. At certain instants of time the microparticles in the SC CO<sub>2</sub> may be distributed randomly in the virtual plane  $P$  and give diffraction patterns, from which one can evaluate the average size of water microdrops in the SC CO<sub>2</sub>.

Let us estimate the water drop size for the diffraction pattern shown in Fig. 3. Here, the laser beam of oval shape (major diameter 3 mm, minor diameter 2 mm), escaping from the source 6 (Fig. 2) is scattered by the water drops

The HPC contents were investigated using the diffraction patterns induced by the scattered laser radiation. A red laser diode-based pointer of  $< 1$  mW power that generates radiation in the wavelength range  $\lambda = 655.7 \pm 2.5$  nm was used as a laser beam source.

Water-phase laser diffractometry experiments were performed in the following order.

A filter paper, soaked in 0.5 ml of distilled water, was placed in the SFE-U reactor. According to the quality certificate, the original water content in carbon dioxide at standard conditions (pressure 101.3 kPa, temperature 20°C) was less than 0.076 g/m<sup>3</sup>. The estimates show that at pressures up to 16.0 MPa the proper water content in CO<sub>2</sub> was considerably less than the quantity of water taken up on the filter paper. On attaining the required reactor pressure and after the 5 min dwell time, a part of the fluid was forwarded through the inlet/outlet connection (see Fig. 1) to the optical HPC. The cell fluid with the water solved in it was examined with the red laser. The laser radiation that passed through the cell was directed onto the screen (see Fig. 2). The time-varying diffraction pattern, obtained at a definite pressure, was being shot with a video camera for 5 min. The obtained video was split into separate shots, which represented static diffraction patterns comprising the information on water drop sizes in SC CO<sub>2</sub>.

located in the virtual plane  $P$ . From experimental observations it follows that the laser spot area is great in comparison with the water drop size. Therefore, the influence of the laser radiation spot limitation on the diffraction pattern is neglected.

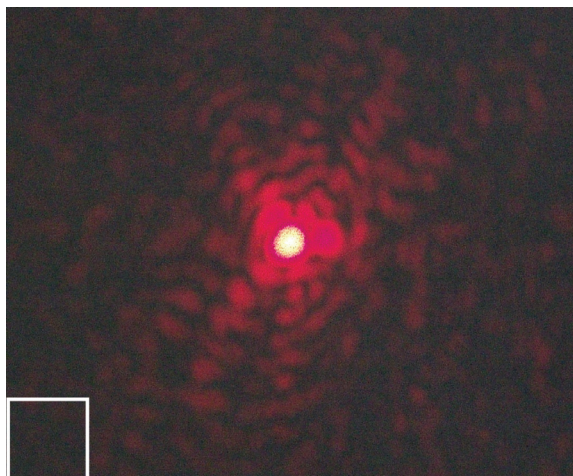


Fig. 3. Image of the static diffraction pattern at a pressure of 10.0 MPa and the 6.0 mm optical path in the HPC.

A white square contour in the left bottom corner with a lateral length of 10.0 mm is given for evaluating the diffraction pattern element dimensions.

The superposition of different quantities of water microdrops, which are projected onto the plane  $P$  on the principle of belonging to one and the same laser beam, will create an inhomogeneously illuminated surface, i.e., at the greatest quantities of water drops give the highest intensity of illumination, and at the least quantities - the lowest illumination. In the ideal case, the regions of maximum illuminance correspond to concentric superposition of water drops, while the lowest-illumination regions correspond to the absence of this superposition. So, laser radiation should scatter on the plane with randomly arranged circles of diameter  $d$ , where  $d$  is the diameter of spherical water drop projection onto the plane  $P$ . In this case, the diffraction pattern must look like a bright circle at the center, surrounded by a sequence of dark and light rings [13]. The bright circle at the center has an angular radius

$$\vartheta \approx \frac{D}{2L} = 1,22 \frac{\lambda}{d}.$$

Hence, one would think that this provides a simple evaluation of the water drop size as

$$d = 2,44 \frac{\lambda L}{D}.$$

In actual fact, at the periphery of Fig. 3 one can see rows of spots that form a certain quantity of radial rays, about 12 to 14 in number. This fact is the evidence that diffraction occurs not on randomly arranged circles, but on their pileup forming a rectilinear polygon with  $n$  sides. At that, it is known that the number of rays is always even, i.e.,  $2n$  [14]. Reasoning from this, we determine the average  $d$  value. For the purpose, we assume that, at least, two inscribed circular projections of water drops fall on one side of the polygon (a greater number of them smoothes-off the angles and makes the rays disappear). Then, by setting the perimeter of the bright circle in the diffraction pattern (Fig. 3) equal to the polygon perimeter with inscribed  $2n$  circles of diameter  $d$  we find the average drop size:

$$d \approx 2,44\pi \frac{\lambda L}{2nD} \quad (1)$$

Substituting the experimental data into expression (1), we evaluate the average size as  $d = 45 \div 50 \mu\text{m}$ .

#### Optical micrometry evaluation of water microdrop dimensions

To verify the results obtained by the laser methods, we have also examined the eluent discharged into the HPC, using a 32-power optical microscope. In this case, instead of the microscope slide we placed the HPC in such a way that the sapphire window area should be orthogonal to the microscope-head optical axis. For the analysis of water phase state, an oblique flare with a wide light beam was used provided that the light source should not get into the field of viewing, and the eluent was against a dark background.

As a result of direct optical observations it has been established that the water dissolved in the SC  $\text{CO}_2$  at a pressure of 10 MPa and a temperature of  $40^\circ\text{C}$  exists in the form of microdrops. According to optical microscope measurements the diameter of these microdrops was estimated to be  $55 \pm 3 \mu\text{m}$ .

So, the experimental investigation into the existence of phases in the two-phase water-SC  $\text{CO}_2$  system has demonstrated that the water is characterized by the limit of solubility in the SC  $\text{CO}_2$ , i.e., the molar fraction of dissolved water is constant with an increase in pressure.

The water in the SC  $\text{CO}_2$  exists in the form of microdrops, the diameter of which, for example, at a pressure of 10 MPa and a temperature of  $40^\circ\text{C}$  is found to be about  $50 \mu\text{m}$ . It is evident that the droplet diameter decreases with an increase in pressure.

#### ANALYSIS OF THE PARAMETERS OF NANOSIZED URANIUM COMPLEXES AND THEIR SOLUBILITY IN WATER. FORMATION OF ASSOCIATES

For an understanding of the kinetics of uranium extraction to the SC  $\text{CO}_2$  medium it is necessary to decide the following issues: to determine the structure of the resulting uranyl nitrate+TBP (uranyl nitrate+ $(\text{C}_4\text{H}_9\text{O})_3\text{PO}$ ) complex, and to describe possible ways of associate formation from that sort of complexes.

In spite of the existence of a sufficient number of publications on the matter (e.g., see [15, 16]), the problems still



remain to be solved.

Thus, it has been shown in [15, 16] that the  $\text{HNO}_3 + \text{TBP}$  complex efficiently extracts uranium to the SC  $\text{CO}_2$  medium. The complex reacts with uranium oxide to form the  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  compound, which is extracted to the SC  $\text{CO}_2$ . Figure 4 and Table give the structure and the values of coupling parameters of the complexes formed by uranyl nitrate with water and triethyl phosphate (TEP), respectively [17].

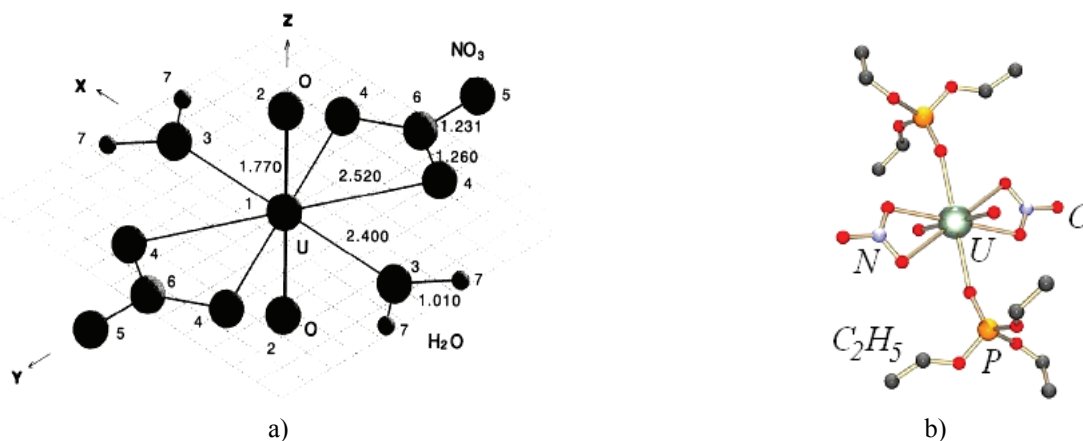


Fig. 4. Schematic diagrams of complex structures  
a)  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ , b)  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TEP}$  [17, 18]

As it follows from Fig. 4, two water molecules from dehydrate of uranyl nitrate (on the left) are replaced by two TEP ( $\text{C}_6\text{H}_{15}\text{O}_4\text{P}$ ) molecules (on the right). In the  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TEP}$  complex the two TEP molecules freely rotate and can take up any conformation, while the interatomic spacing between U and O atoms (just as for the  $\text{P}=\text{O}$  coupling) is harmonically fixed to the equilibrium distance.

Table

Geometrical characteristics of the  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  complex, [15-20].

Complex	$r_{\text{U}=\text{O}}$ (Å)	$r_{\text{U}-\text{O}_2\text{NO}}$ (Å)	$r_{\text{U}-\text{L}}$ (Å)	$\Theta_{\text{U}-\text{O}-\text{P}}$ (deg)
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	1.77	2.52	2.40	—
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TMP}$	1.78	2.53	2.36	$161 \pm 7$
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$	1.78	2.54	2.41	$172 \pm 10$

It is known that TBP shows a relatively low solubility in the aqueous phase [21]. It represents a compound ether of phosphoric acid and butanol, which can hydrolyze, for example, in acidic medium. In acidic aqueous solutions there occurs breaking of carbon-to-oxygen bonds of TBP with gradual abstraction of butanol molecules and formation of dibutyl phosphate (DBP), monobutyl phosphate (MBP) and, eventually, phosphoric acid. It should be noted that MBP forms with uranium the compound, which shows a strong aqueous phase affinity. The ratio of the formed DBP and MBP is approximately 10:1. The hydrolysis reactions occur in both aqueous and organic phases. The rate of TBP hydrolysis appreciably increases with increase in temperature. For example, as temperature rises from 25 to 40°C, the rate of DBP formation increases by a factor of 5, and with a rise up to 75°C – by a factor of 25.

So, based on the structure of the resulting complex and the temperature conditions of the experiment (40°C), it is believed that the  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{TBP}$  complex can hydrolyze, i.e., may take on diphilic (one TBP molecule of the complex forms the MBP molecule) or fully hydrophilic properties (two TBP molecules of the complex are transformed into the MBP molecule). In this case, because the complex takes on hydrophilic properties in the SC  $\text{CO}_2$  medium comprising water microdrops dissolved in it, the complex will concentrate in the aqueous phase to form supramolecular assemblies [5]. The last ones represent polymolecular associates resulting from spontaneous association of uranium complexes into a specific phase, in our situation, the water microdrop (inverted water micelle [1]).

This concentration apparently leads to the formation of associates in the system, the size of which is determined by the size of water microdrops, and the way of assembling of nanosized complexes still remains to be elucidated. It is evident that the water microdrop represents a microreactor, where the extraction processes occur. A detailed investigation of the structure and properties of these microreactors is of importance for understanding the nature of current processes, and this in total should contribute towards the improved extraction of uranium complexes efficiency into the SC  $\text{CO}_2$  medium.

## CONCLUSIONS

In summary, as a result of studies of the role of water in the formation of associates from nanosized complexes of uranium in a supercritical carbon dioxide (SC CO<sub>2</sub>) medium, it has been established that at given temperature the water exists in the form of microdrops, the diameter of which makes, for example, at a pressure of 10 MPa and a temperature of 40°C, about 50 µm.

It has been noted that at a pressure of 10 MPa and a temperature of 40°C the nanosized UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2TBP complex can take on hydrophilic properties.

As a result of taking on hydrophilic properties, the UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>·2TBP complex will concentrate in water microdrops.

The concentration of the complex in water microdrops leads to the formation of associates in the system, the associate size being determined by the size of water microdrops.

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